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(21) International Application Number: PCT/US89/04282 (22) International Filing Date: 29 September 1989 (29.09.89) (71) Applicant: CHEVRON RESEARCH COMPANY [US/ US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US). (72) Inventor: RUHE, William, R., Jr. ; 895 Rose Drive, Ben- icia, CA 94510 (US). (74) Agents: CAROLI, Claude, J. et al.; Chevron Corporation, Law Department, P.O. Box 7141, San Francisco, CA 94120-7141 (US). (81) Designated States: AT (European patent), AU, BE (Euro- pean patent), BR, CH (European patent), DE (European patent)*, DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).		Published <i>With international search report.</i>
(54) Title: PROCESS FOR PREPARING POLYMERIC DISPERSANTS HAVING ALTERNATING POLYALKYLENE AND SUCCINIC GROUPS (57) Abstract A process for preparing an oligomeric copolymer of an unsaturated acidic reactant and a high molecular weight olefin hav- ing a sufficient number of carbon atoms such that the resulting copolymer is soluble in lubricating oil and wherein at least 20 weight percent of the total olefin comprises an alkylvinylidene isomer, which process comprises reacting the high molecular weight olefin with the unsaturated acidic reactant in the presence of a solvent which comprises the reaction product of an unsatu- rated acidic reactant and a high molecular weight olefin.		

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01 PROCESS FOR PREPARING POLYMERIC DISPERSANTS
02 HAVING ALTERNATING POLYALKYLENE AND SUCCINIC GROUPS
03

04 BACKGROUND OF THE INVENTION
05

06 The present invention relates to a process for preparing
07 compositions which are useful as intermediates for dis-
08 persants used in lubricating oil compositions or as dis-
09 persants themselves. In addition, some of the compositions
10 prepared by the present process are useful in the pre-
11 paration of high molecular weight dispersants which have
12 superior dispersant properties for dispersing sludge and
13 varnish and superior Viton Seal compatibility. Such high
14 molecular weight dispersants also advantageously impart
15 fluidity modifying properties to lubricating oil composi-
16 tions which are sufficient to allow elimination of some
17 proportion of viscosity index improver from multigrade
18 lubricating oil compositions which contain these
19 dispersants.

20
21 It is known in the art that alkenyl-substituted succinic
22 anhydrides have been used as dispersants. Such alkenyl-
23 substituted succinic anhydrides have been prepared by two
24 different processes, a thermal process (see, e.g., U.S.
25 Patent No. 3,361,673) and a chlorination process (see, e.g.,
26 U.S. Patent No. 3,172,892). The polyisobutenyl succinic
27 anhydride ("PIBSA") produced by the thermal process has been
28 characterized as a monomer containing a double bond in the
29 product. Although the exact structure of chlorination PIBSA
30 has not been definitively determined, the chlorination
31 process PIBSA materials have been characterized as monomers
32 containing either a double bond, a ring other than a
33 succinic anhydride ring and/or chlorine in the product.
34 [See J. Weill and B. Sillion, "Reaction of Chlorinated

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01 Polyisobutene with Maleic Anhydride: Mechanism Catalysis by
02 Dichloromaleic Anhydride", Revue de l'Institut Français du
03 Petrole, Vol. 40, No. 1, pp. 77-89 (January-February,
04 1985).] Such compositions include one-to-one monomeric
05 adducts (see, e.g., U.S. Patents Nos. 3,219,666; 3,381,022)
06 as well as adducts having polyalkenyl-derived substituents
07 adducted with at least 1.3 succinic groups per polyalkenyl-
08 derived substituent (see, e.g., U.S. Patent No. 4,234,435).
09

10 In addition, copolymers of maleic anhydrides and some ali-
11 phatic alpha-olefins have been prepared. The polymers so
12 produced were useful for a variety of purposes including
13 dispersants for pigments and intermediates in the prepara-
14 tion of polyesters by their reaction with polyols or poly-
15 epoxides. However, olefins having more than about 30 carbon
16 atoms were found to be relatively unreactive. (See, e.g.,
17 U.S. Patents Nos. 3,461,108; 3,560,455; 3,560,456;
18 3,560,457; 3,580,893; 3,706,704; 3,729,450; and 3,729,451).
19

20 Commonly assigned copending U.S. patent application Serial
21 No. 251,613, to James J. Harrison, filed September 29, 1988,
22 entitled "Novel Polymeric Dispersants Having Alternating
23 Polyalkylene and Succinic Groups" discloses copolymers pre-
24 pared by reacting an unsaturated acidic reactant, such as
25 maleic anhydride, with a high molecular weight olefin, such
26 as polyisobutene, in the presence of a free radical initia-
27 tor, wherein at least about 20 percent of the total high
28 molecular weight olefin comprises an alkylvinylidene isomer
29 and wherein the high molecular weight olefin has a suffi-
30 cient number of carbon atoms such that the resulting copolymer
31 is soluble in lubricating oil. In U.S. Serial No. 251,613,
32 it is also taught that the reaction may be conducted neat or
33 in the presence of a solvent in which the reactants and free
34 radical initiator are soluble. Suitable solvents disclosed

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01 in U.S. Serial No. 251,613 include liquid saturated or
02 aromatic hydrocarbons having from 6 to 20 carbon atoms,
03 ketones having from 3 to 5 carbon atoms and liquid saturated
04 aliphatic dihalogenated hydrocarbons havng from 1 to 5
05 carbon atoms. Examples of solvents taught in U.S. Serial
06 No. 251,613 are acetone, tetrahydrofuran, chloroform,
07 methylene chloride, dichloroethane, toluene, dioxane,
08 chlorobenzene and xylene.

09

10 The use of halogenated hydrocarbons as a solvent in the
11 reaction of unsaturated acidic reactants, such as maleic
12 anhydride, and high molecular weight olefins of the type
13 described in U.S. Serial No. 251,613 has a number of
14 disadvantages. Such solvents are expensive, they are
15 environmentally undesirable and they impede recycling of
16 lubricating oils because of the residual halogen content.

17

18 In the above-described reaction, the solvent is used
19 primarily to solubilize the unsaturated acidic reactant, but
20 also serves to reduce the viscosity of the reaction mixture.
21 Unsaturated acidic reactants such as maleic anhydride are
22 not very soluble in high molecular weight olefins at typical
23 reaction temperatures of 50°C to 210°C. When the unsatu-
24 rated acidic reactant is maleic anhydride, it has been found
25 that if the maleic anhydride forms a separate phase due to
26 poor solubility, not only is the reaction rate negatively
27 affected, but an undesirable resin or tar-like substance is
28 formed which is believed to be polymaleic anhydride. Conse-
29 quently, it would be highly advantageous to provide a pro-
30 cess which avoids this condition, without having to resort
31 to a halogenated hydrocarbon solvent.

32

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SUMMARY OF THE INVENTION

01
02
03 The present invention is directed to a process for preparing
04 an oligomeric copolymer of an unsaturated acidic reactant
05 and a high molecular weight olefin having a sufficient num-
06 ber of carbon atoms such that the resulting copolymer is
07 soluble in lubricating oil and wherein at least 20 weight
08 percent of the total olefin comprises an alkylvinylidene
09 isomer, which process comprises reacting the high molecular
10 weight olefin with the unsaturated acidic reactant in the
11 presence of a free radical initiator and a solvent which
12 comprises the reaction product of an unsaturated acidic
13 reactant and a high molecular weight olefin. Preferably,
14 the solvent comprises (a) an oligomeric copolymer of an
15 unsaturated acidic reactant and a high molecular weight
16 olefin; or (b) a monomeric adduct of an unsaturated acidic
17 reactant and a high molecular weight olefin in at least a
18 one to one mole ratio of acidic reactant to olefin; or a
19 mixture thereof.
20
21 The copolymers produced by the present process have alter-
22 nating succinic and polyalkylene groups. Suitable olefins
23 for use in preparing these copolymers include those having
24 about 32 carbon atoms or more, preferably having about 52
25 carbon atoms or more. Those preferred high molecular weight
26 olefins include polyisobutenes. Especially preferred ole-
27 fins for use in preparing the copolymer products are poly-
28 isobutenes having average molecular weights of from about
29 500 to about 5000 and in which the alkylvinylidene isomer
30 comprises at least 50 percent of the total olefin.
31
32 The copolymers prepared by the process of the invention are
33 useful as dispersants themselves and also as intermediates
34 in the preparation of other dispersant additives having

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01 improved dispersancy and/or detergency properties when
02 employed in a lubricating oil. These copolymers are also
03 advantageous because they do not contain double bonds, rings
04 other than succinic anhydride rings, or chlorine (in
05 contrast to thermal and chlorination PIBSAs) and as such
06 have improved stability, as well as improved environmental
07 properties due to the absence of chlorine.

08
09 The copolymers produced by the instant process can also be
10 used to form polysuccinimides which are prepared by reacting
11 the copolymer with a polyamine to give a polysuccinimide.
12 Such polysuccinimides include mono-polysuccinimides (where a
13 polyamine component reacts with one succinic group); bis-
14 polysuccinimides (where a polyamine component reacts with a
15 succinic group from each of two copolymer molecules, thus
16 effectively cross-linking the copolymer molecules); and
17 higher polysuccinimides (where a polyamine component reacts
18 with a succinic group from each of greater than 2 copolymer
19 molecules). These polysuccinimides are useful as disper-
20 sants and/or detergents in fuels and oils. In addition,
21 these polysuccinimides have advantageous viscosity modifying
22 properties, and may provide a viscosity index credit
23 ("V.I. Credit") when used in lubricating oils, which may
24 permit elimination of some portion of viscosity index
25 improver ("V.I. Improver") from multigrade lubricating oils
26 containing the same.

27
28 In addition, such polysuccinimides can form a ladder poly-
29 meric structure or a cross-linked polymeric structure.
30 These structures are advantageous because it is believed
31 such structures are more stable and resistant to hydrolytic
32 degradation and also to degradation by shear stress.

33
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01 Moreover, the copolymers prepared by the present process can
02 be employed to make modified polysuccinimides wherein one or
03 more of the nitrogens of the polyamine component is sub-
04 stituted with a hydrocarbyl oxycarbonyl, a hydroxyhydrocar-
05 byl oxycarbonyl or a hydroxy poly(oxyalkylene)-oxycarbonyl.
06 These modified polysuccinimides are improved dispersants
07 and/or detergents for use in fuels or oils.

08

09 Accordingly, the copolymers made by the present process are
10 useful in providing a lubricating oil composition comprising
11 a major amount of an oil of lubricating viscosity and an
12 amount of a copolymer, polysuccinimide or modified succini-
13 mide additive sufficient to provide dispersancy and/or
14 detergency. These additives may also be formulated in
15 lubricating oil concentrates which comprise from about 90 to
16 about 50 weight percent of an oil of lubricating viscosity
17 and from about 10 to about 50 weight percent of the
18 additive.

19

20 Furthermore, the copolymers formed by the present process
21 can be used to provide a fuel composition comprising a major
22 portion of a fuel boiling in a gasoline or diesel range and
23 an amount of copolymer, polysuccinimide or modified succini-
24 mide additives sufficient to provide dispersancy and/or
25 detergency. These additives can also be used to make fuel
26 concentrates comprising an inert stable oleophilic organic
27 solvent boiling in the range of about 150°F to about 400°F
28 and from about 5 to about 50 weight percent of such
29 additive.

30

31 Definitions

32

33 As used herein, the following terms have the following
34 meanings unless expressly stated to the contrary.

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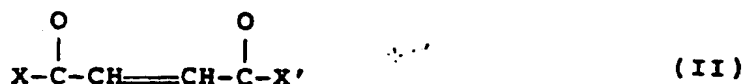
01 The term "unsaturated acidic reactants" refers to maleic or
 02 fumaric reactants of the general formula:

03

04

05

06



07 wherein X and X' are the same or different, provided that at
 08 least one of X and X' is a group that is capable of reacting
 09 to esterify alcohols, form amides or amine salts with ammo-
 10 nia or amines, form metal salts with reactive metals or
 11 basically reacting metal compounds and otherwise function as
 12 acylating agents. Typically, X and/or X' is -OH, -O-hydro-
 13 carbyl, -OM⁺ where M⁺ represents one equivalent of a metal,
 14 ammonium or amine cation, -NH₂, -Cl, -Br, and taken together
 15 X and X' can be -O- so as to form an anhydride. Preferably
 16 X and X' are such that both carboxylic functions can enter
 17 into acylation reactions. Maleic anhydride is a preferred
 18 unsaturated acidic reactant. Other suitable unsaturated
 19 acidic reactants include electron-deficient olefins such as
 20 monophenyl maleic anhydride; monomethyl, dimethyl, mono-
 21 chloro, monobromo, monofluoro, dichloro and difluoro maleic
 22 anhydride; N-phenyl maleimide and other substituted
 23 maleimides; isomaleimides; fumaric acid, maleic acid, alkyl
 24 hydrogen maleates and fumarates, dialkyl fumarates and
 25 maleates, fumaronilic acids and maleanic acids; and
 26 maleonitrile, and fumaronitrile.

27

28 The term "alkylvinylidene" or "alkylvinylidene isomer"
 29 refers to high molecular weight olefins and polyalkylene
 30 components having the following vinylidene structure

31

32

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01 wherein R is alkyl or substituted alkyl of sufficient chain
02 length to give the resulting molecule solubility in
03 lubricating oils and fuels, thus R generally has at least
04 about 30 carbon atoms, preferably at least about 50 carbon
05 atoms and R_v is lower alkyl of about 1 to about 6 carbon
06 atoms.

07

08 The term "soluble in lubricating oil" refers to the ability
09 of a material to dissolve in aliphatic and aromatic hydro-
10 carbons such as lubricating oils or fuels in essentially all
11 proportions.

12

13 The term "high molecular weight olefins" refers to olefins
14 (including polymerized olefins having a residual unsatura-
15 tion) of sufficient molecular weight and chain length to
16 lend solubility in lubricating oil to their reaction prod-
17 ucts. Typically olefins having about 32 carbons or greater
18 (preferably olefins having about 52 carbons or more)
19 suffice.

20

21 The term "high molecular weight polyalkyl" refers to poly-
22 alkyl groups of sufficient molecular weight and hydrocarbyl
23 chain length that the products prepared having such groups
24 are soluble in lubricating oil. Typically these high
25 molecular weight polyalkyl groups have at least about 30
26 carbon atoms, preferably at least about 50 carbon atoms.
27 These high molecular weight polyalkyl groups may be derived
28 from high molecular weight olefins.

29

30 The term "PIBSA" is an abbreviation for polyisobutenyl
31 succinic anhydride.

32

33 The term "polyPIBSA" refers to a class of copolymers within
34 the scope of the present invention which are copolymers of

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01 polyisobutene and an unsaturated acidic reactant which have
 02 alternating succinic groups and polyisobutyl groups.
 03 PolyPIBSA has the general formula

04

05

06

07

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09

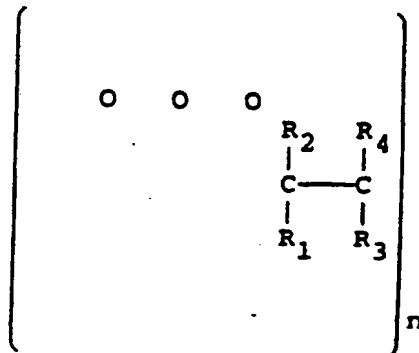
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11

12

13

14



15 wherein n is one or greater; R₁, R₂, R₃ and R₄ are selected from
 16 hydrogen, methyl and polyisobutyl having at least about 30 carbon
 17 atoms (preferably at least about 50 carbon atoms) wherein either
 18 R₁ and R₂ are hydrogen and one of R₃ and R₄ is methyl and the
 19 other is polyisobutyl, or R₃ and R₄ are hydrogen and one of R₁
 20 and R₂ is methyl and the other is polyisobutyl.

21

22 The term "PIBSA number" refers to the anhydride (succinic group)
 23 content of polyPIBSA on a 100% actives basis. The PIBSA number
 24 is calculated by dividing the saponification number by the per-
 25 cent polyPIBSA in the product. The units are mg KOH per gram
 26 sample.

27

28 The term "succinic group" refers to a group having the formula

29

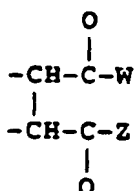
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01 wherein W and Z are independently selected from the group
02 consisting of -OH, -Cl, -O- lower alkyl or taken together
03 are -O- to form a succinic anhydride group. The term "-O-
04 lower alkyl" is meant to include alkoxy of 1 to 6 carbon
05 atoms.

06

07 The term "degree of polymerization" expresses the length of
08 a linear polymer and refers to the number of repeating
09 (monomeric) units in the chain. The average molecular
10 weight of a polymer is the product of the degree of polymer-
11 ization and the average molecular weight of the repeating
12 unit (monomer). Accordingly, the average degree of poly-
13 merization is calculated by dividing the average molecular
14 weight of the polymer by the average molecular weight of the
15 repeating unit.

16

17 The term "polysuccinimide" refers to the reaction product of
18 a copolymer made by the present process with polyamine.

19

20

21

DETAILED DESCRIPTION OF THE INVENTION

22

23

A. COPOLYMER

24

25 The copolymers made by the present process are prepared by
26 reacting a high molecular weight olefin wherein at least
27 about 20% of the total olefin composition comprises the
28 alkylvinylidene isomer and an unsaturated acidic reactant in
29 the presence of a free radical initiator and a solvent com-
30 prising the reaction product of an unsaturated acidic
31 reactant and a high molecular weight olefin. Preferably,
32 the solvent comprises (a) an oligomeric copolymer of an
33 unsaturated acidic reactant and a high molecular weight
34 olefin or (b) a monomeric adduct of an unsaturated acidic

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01 reactant and a high molecular weight olefin in at least a
02 one to one mole ratio of acidic reactant to olefin; or a
03 mixture thereof. Suitable high molecular weight olefins
04 have a sufficient number of carbon atoms so that the
05 resulting copolymer is soluble in lubricating oil and thus
06 have on the order of about 32 carbon atoms or more. Pre-
07 ferred high molecular weight olefins are polyisobutenes and
08 polypropylenes. Especially preferred are polyisobutenes,
09 particularly preferred are those having a molecular weight
10 of about 500 to about 5000, more preferably about 900 to
11 about 2500. Preferred unsaturated acidic reactants include
12 maleic anhydride.

13
14 Since the high molecular weight olefins used in the process
15 of the present invention are generally mixtures of indi-
16 vidual molecules of different molecular weights, individual
17 copolymer molecules resulting will generally contain a mix-
18 ture of high molecular weight polyalkyl groups of varying
19 molecular weight. Also, mixtures of copolymer molecules
20 having different degrees of polymerization will be produced.
21

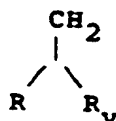
22 The copolymers made by the process of the present invention
23 have an average degree of polymerization of 1 or greater,
24 preferably from about 1.1 to about 20, and more preferably
25 from about 1.5 to about 10.

26
27 In accordance with the process of the present invention, the
28 desired copolymer products are prepared by reacting a "reac-
29 tive" high molecular weight olefin in which a high propor-
30 tion of unsaturation, at least about 20%, is in the
31 alkylvinylidene configuration, e.g.,

32
33
34

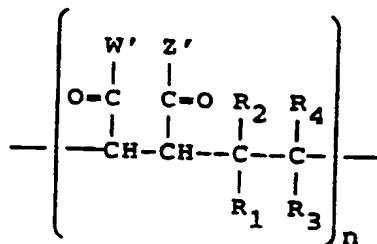
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wherein R and R_V are as previously defined in conjunction with Formula III, with an unsaturated acidic reactant in the presence of a free radical initiator and an oligomeric or monomeric solvent as described above. The product copolymer has alternating polyalkylene and succinic groups and has an average degree of polymerization of 1 or greater.

The copolymers prepared by the instant process have the general formula:

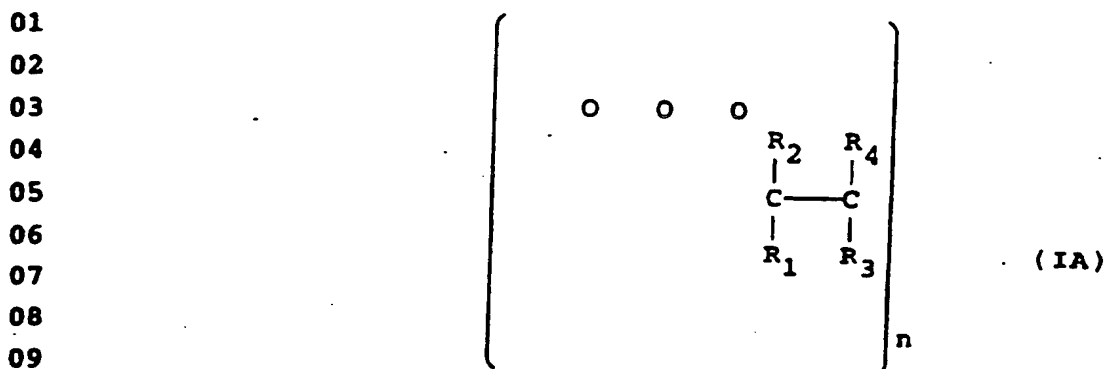


wherein W' and Z' are independently selected from the group consisting of -OH, -O- lower alkyl or taken together are -O- to form a succinic anhydride group, n is one or greater; and R₁, R₂, R₃ and R₄ are selected from hydrogen, lower alkyl of 1 to 6 carbon atoms, and high molecular weight polyalkyl wherein either R₁ and R₂ are hydrogen and one of R₃ and R₄ is lower alkyl and the other is high molecular weight polyalkyl, or R₃ and R₄ are hydrogen and one of R₁ and R₂ is lower alkyl and the other is high molecular weight polyalkyl.

In a preferred embodiment, when maleic anhydride is used as the unsaturated acidic reactant, the reaction produces copolymers predominately of the following formula:

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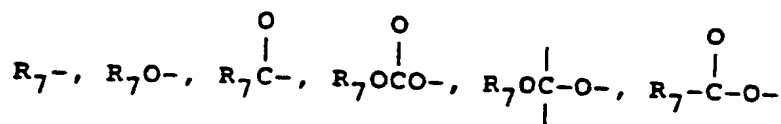
11 wherein n is about 1 to about 100, preferably about 2 to
12 about 20, more preferably 2 to 10, and R₁, R₂, R₃ and R₄ are
13 selected from hydrogen, lower alkyl of about 1 to 6 carbon
14 atoms and higher molecular weight polyalkyl, wherein either
15 R₁ and R₂ are hydrogen and one of R₃ and R₄ is lower alkyl
16 and the other is high molecular weight polyalkyl or R₃ and
17 R₄ are hydrogen and one of R₁ and R₂ is lower alkyl and the
18 other is high molecular weight polyalkyl.
19

20
21 Preferably, the high molecular weight polyalkyl group has at
22 least about 30 carbon atoms, preferably at least about 50
23 carbon atoms. Preferred high molecular weight polyalkyl
24 groups include polyisobutyl groups. Preferred polyisobutyl
25 groups include those having average molecular weights of
26 about 500 to about 5000, more preferably from about 900 to
27 about 2500. Preferred lower alkyl groups include methyl and
28 ethyl; especially preferred lower alkyl groups include
29 methyl.

30 Generally, such copolymers contain an initiator group, I,
31 and a terminator group, T, as a result of the reaction with
32 the free radical initiator used in the polymerization
33 reaction. In such a case, the initiator and terminator
34 groups may be

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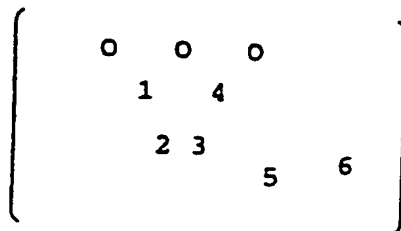
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where R_7 is hydrogen, alkyl, aryl, alkaryl, cycloalkyl, alkoxy, cycloalkoxy, acyl, alkenyl, cycloalkenyl, alkynyl, or alkyl, aryl or alkaryl optionally substituted with 1 to 4 substituents independently selected from nitrile, keto, halogen, nitro, alkyl, aryl, and the like. Alternatively, the initiator group and/or terminator group may be derived from the reaction product of the initiator with another material, such as solvent.

The copolymers prepared by the present process differ from the PIBSAs prepared by the thermal process in that the thermal process products contain a double bond and a singly substituted succinic anhydride group, that is, a monomeric one to one adduct. The copolymers prepared by the present process differ from the PIBSAs prepared by the chlorination process, since those products contain a double bond, a ring other than a succinic anhydride ring, or one or more chlorine atoms.

The copolymers prepared by the present process contain no double bonds, rings other than succinic anhydride rings, or chlorine atoms. In addition, the succinic anhydride groups are doubly substituted (i.e., have two substituents, one of which may be hydrogen) at the 2- and 3-positions, that is:



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01 A(1) High Molecular Weight Polyalkylene Group

02

03 The high molecular weight polyalkyl group is derived from a
04 high molecular weight olefin. The high molecular weight
05 olefins used in the preparation of the instant copolymers
06 are of sufficiently long chain length so that the resulting
07 composition is soluble in and compatible with mineral oils,
08 fuels and the like; and the alkylvinylidene isomer of the
09 high molecular weight olefin comprises at least about 20% of
10 the total olefin composition.

11

12 Such high molecular weight olefins are generally mixtures of
13 molecules having different molecular weights and can have at
14 least one branch per 6 carbon atoms along the chain, pre-
15 ferably at least one branch per 4 carbon atoms along the
16 chain, and particularly preferred that there be about one
17 branch per 2 carbon atoms along the chain. These branched
18 chain olefins may conveniently comprise polyalkenes prepared
19 by the polymerization of olefins of from 3 to 6 carbon
20 atoms, and preferably from olefins of from 3 to 4 carbon
21 atoms, and more preferably from propylene or isobutylene.
22 The addition-polymerizable olefins employed are normally
23 1-olefins. The branch may be of from 1 to 4 carbon atoms,
24 more usually of from 1 to 2 carbon atoms and preferably
25 methyl.

26

27 The preferred alkylvinylidene isomer comprises a methyl- or
28 ethylvinylidene isomer, more preferably the methylvinylidene
29 isomer.

30

31 The especially preferred high molecular weight olefins used
32 to prepare the instant copolymers are polyisobutenes which
33 comprise at least about 20% of the more reactive methyl-
34 vinylidene isomer, preferably at least 50% and more

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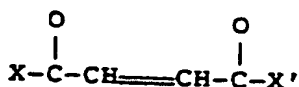
01 preferably at least 70%. Suitable polyisobutenes include
02 those prepared using BF_3 catalysis. The preparation of such
03 polyisobutenes in which the methylvinylidene isomer com-
04 prises a high percentage of the total composition is
05 described in U.S. Patents Nos. 4,152,499 and 4,605,808.
06

07 Polyisobutenes produced by conventional AlCl_3 catalysis when
08 reacted with unsaturated acidic reactants, such as maleic
09 anhydride, in the presence of a free radical initiator, pro-
10 duce products similar to thermal PIBSA in molecular weight
11 and thus do not produce a copolymeric product.
12

13 Preferred are polyisobutenes having average molecular
14 weights of about 500 to about 5000. Especially preferred
15 are those having average molecular weights of about 900 to
16 about 2500.
17

18 A(2) Unsaturated Acidic Reactant

19
20 The unsaturated acidic reactant used in the preparation of
21 the instant copolymers comprises a maleic or fumaric
22 reactant of the general formula:
23



27 wherein X and X' are the same or different, provided that at
28 least one of X and X' is a group that is capable of reacting
29 to esterify alcohols, form amides or amine salts with ammo-
30 nia or amines, form metal salts with reactive metals or
31 basically reacting metal compounds and otherwise function to
32 acylate. Typically, X and/or X' is -OH, -O-hydrocarbyl,
33 -OM⁺ where M⁺ represents one equivalent of a metal, ammonium
34 or amine cation, -NH₂, -Cl, -Br, and taken together X and X'

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01 can be -O- so as to form an anhydride. Preferably, X and X'
02 are such that both carboxylic functions can enter into
03 acylation reactions. Preferred are acidic reactants where X
04 and X' are each independently selected from the group con-
05 sisting of -OH, -Cl, -O- lower alkyl and when taken
06 together, X and X' are -O-. Maleic anhydride is the pre-
07 ferred acidic reactant. Other suitable acidic reactants
08 include electron-deficient olefins such as monophenyl maleic
09 anhydride; monomethyl, dimethyl, monochloro, monobromo,
10 monofluoro, dichloro and difluoro maleic anhydride; N-phenyl
11 maleimide and other substituted maleimides; isomaleimides;
12 fumaric acid, maleic acid, alkyl hydrogen maleates and
13 fumarates, dialkyl fumarates and maleates, fumaronilic acids
14 and maleanic acids; and maleonitrile, and fumaronitrile.
15

16 Preferred unsaturated acidic reactants include maleic
17 anhydride, and maleic acid. The particularly preferred
18 acidic reactant is maleic anhydride.
19

20 A(3) General Preparation of Copolymer

21

22 As noted above, the copolymers made by the process of the
23 invention are prepared by reacting a reactive high molecular
24 weight olefin and an unsaturated acidic reactant in the
25 presence of a free radical initiator and a specific solvent,
26 as described herein.
27

28 As discussed above, in U.S. Patent Application Serial
29 No. 251,613 it is taught that the reaction of high molecular
30 weight olefin and unsaturated acidic reactant in the
31 presence of a free radical initiator may be conducted neat
32 or with a solvent, such as a saturated or aromatic hydro-
33 carbon, a ketone or a liquid saturated aliphatic
34 dihalogenated hydrocarbon.

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01 It has now been found that when this reaction is carried out
02 neat, that is, in the absence of any solvent, a significant
03 amount of resin is formed, presumably from polymerization of
04 the unsaturated acidic reactant.

05

06 This problem can be somewhat avoided by employing a
07 halogenated hydrocarbon solvent, but the use of such sol-
08 vents also has certain drawbacks. Halogenated hydrocarbon
09 solvents are both expensive and environmentally undesirable.
10 Moreover, they impede the recycling of lubricating oils
11 because of the residual halogen content.

12

13 It has now been discovered that oligomeric copolymers of
14 high molecular weight olefins and unsaturated acidic reac-
15 tants can be prepared in improved yields by employing a
16 solvent which comprises the reaction product of an
17 unsaturated acidic reactant and a high molecular weight
18 olefin. Preferably, the solvent comprises either (a) an
19 oligomeric copolymer of an unsaturated acidic reactant and a
20 high molecular weight olefin or (b) a monomeric adduct of an
21 unsaturated acidic reactant and a high molecular weight
22 olefin in at least a one-to-one mole ratio of acidic
23 reactant to olefin. Mixtures of (a) and (b) may also be
24 employed as the solvent.

25

26 For use as a solvent, the oligomeric copolymer of
27 unsaturated acidic reactant and high molecular weight olefin
28 can be conveniently obtained by retaining a portion of the
29 oligomeric copolymer product from a previous run. Alterna-
30 tively, the solvent may be a monomeric adduct of an
31 unsaturated acidic reactant and a high molecular weight
32 olefin in at least a 1:1 ratio of acid to olefin, which can
33 be readily prepared via the known "thermal process" or the
34 known "chlorination process", as described above. For use

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01 in preparing the monomeric adduct, the high molecular weight
02 olefin may contain less than 20% of the alkylvinylidene
03 isomer.

04

05 Preferred solvents include the oligomeric copolymer product
06 of maleic anhydride and polyisobutene, that is, "polyPIBSA",
07 as defined above, and the monomeric adduct of maleic
08 anhydride and polyisobutene, namely, polyisobutenyl succinic
09 anhydride or "PIBSA". A particularly preferred solvent is
10 polyPIBSA.

11

12 The "thermal" PIBSA described above is well known in the
13 art. One method of preparing thermal PIBSA is disclosed in
14 U.S. Patent No. 3,361,673, the disclosure of which is
15 incorporated herein by reference for its teachings on
16 preparing thermal PIBSA. The "chlorination process" PIBSA
17 described above is also well known in the art. One method
18 of preparing chlorination process PIBSA is disclosed in
19 U.S. Patent No. 3,172,892, the disclosure of which is
20 incorporated herein by reference for its teachings in
21 preparing chlorination process PIBSA.

22

23 The amount of solvent employed should be such that it can
24 dissolve the acidic reactant and the high molecular weight
25 olefin, in addition to the resulting copolymers. The volume
26 ratio of solvent to high molecular weight olefin is suitably
27 between 1:1 and 100:1, and is preferably between 1.5:1 and
28 4:1.

29

30 The reaction may be conducted at a temperature in the range
31 of about 90°C to about 210°C, and preferably from about
32 130°C to about 150°C. Reaction at lower temperatures works
33 to a point, but the reaction solution generally becomes
34 viscous and therefore requires added heat to obtain

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01 satisfactory reaction. Although not wishing to be bound by
02 any theory, it is believed that there is a so-called "cage-
03 effect", wherein the free radical initiator is trapped in
04 the solvent/reaction mixture and therefore cannot
05 effectively initiate the polymerization reaction.
06

07 Although it has been observed that reaction may be slow or
08 incomplete below the preferred temperature range of about
09 130°C to 150°C, it is envisioned that stepping the reaction
10 temperature up in increments from a minimum of about 90°C
11 could provide advantageous results. The highest temperature
12 of these incremental temperature steps is preferably above
13 about 140°C when complete reaction is desired.
14

15 In general, the copolymerization process of the present
16 invention can be initiated by any free radical initiator.
17 Such initiators are well known in the art. However, the
18 choice of free radical initiator may be influenced by the
19 reaction temperature employed.
20

21 The preferred free-radical initiators are the peroxide-type
22 polymerization initiators and the azo-type polymerization
23 initiators. Radiation can also be used to initiate the
24 reaction, if desired.
25

26 The peroxide-type free-radical initiator can be organic or
27 inorganic, the organic having the general formula: R_3OOR_3'
28 where R_3 is any organic radical and R_3' is selected from the
29 group consisting of hydrogen and any organic radical. Both
30 R_3 and R_3' can be organic radicals, preferably hydrocarbon,
31 aroyl, and acyl radicals, carrying, if desired, substituents
32 such as halogens, etc. Preferred peroxides include di-tert-
33 butyl peroxide, tert-butyl peroxybenzoate, and dicumyl
34 peroxide.

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01 Examples of other suitable peroxides, which in no way are
02 limiting, include benzoyl peroxide; lauroyl peroxide; other
03 tertiary butyl peroxides; 2,4-dichlorobenzoyl peroxide;
04 tertiary butyl hydroperoxide; cumene hydroperoxide; diacetyl
05 peroxide; acetyl hydroperoxide; diethylperoxycarbonate;
06 tertiary butyl perbenzoate; and the like.

07

08 The azo-type compounds, typified by alpha, alpha'-azo-bisiso-
09 butyronitrile, are also well-known free-radical promoting
10 materials. These azo compounds can be defined as those
11 having present in the molecule group -N=N wherein the
12 balances are satisfied by organic radicals, at least one of
13 which is preferably attached to a tertiary carbon. Other
14 suitable azo compounds include, but are not limited to,
15 p-bromobenzenediazonium fluoborate; p-tolyldiazoaminoben-
16 zene; p-bromobenzenediazonium hydroxide; azomethane and
17 phenyldiazonium halides. A suitable list of azo-type com-
18 pounds can be found in U.S. Patent No. 2,551,813, issued
19 May 8, 1951 to Paul Pinkney.

20

21 The amount of initiator to employ, exclusive of radiation,
22 of course, depends to a large extent on the particular
23 initiator chose, the high molecular olefin used and the
24 reaction conditions. The initiator must, of course, be
25 soluble in the reaction medium. The usual concentrations of
26 initiator are between 0.001:1 and 0.2:1 moles of initiator
27 per mole of acidic reactant, with preferred amounts between
28 0.005:1 and 0.10:1.

29

30 In carrying out the process of the invention, a single free
31 radical initiator or a mixture of free radical initiators
32 may be employed. The initiator may also be added over time.
33 For example, it may be desirable to add an initiator having
34 a low decomposition temperature as the mixture is warming to

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01 reaction temperature, and then add an initiator having a
02 higher decomposition temperature as the mixture reaches
03 higher reaction temperatures. Alternatively, a combination
04 of initiators could both be added prior to heating and
05 reaction. In this case, an initiator having a high decom-
06 position temperature would initially be inert, but would
07 later become active as the temperature rose.

08
09 The reaction pressure should be sufficient to minimize
10 losses of acidic reactant to the vapor phase. Pressures can
11 therefore vary between about atmospheric and 100 psig or
12 higher, but the preferred pressure is atmospheric.

13
14 The reaction time is usually sufficient to result in the
15 substantially complete conversion of the acidic reactant and
16 high molecular weight olefin to copolymer. The reaction
17 time is suitable between one and 24 hours, with preferred
18 reaction times between two and ten hours.

19
20 As noted above, the subject reaction is a solution-type
21 polymerization reaction. The high molecular weight olefin,
22 acidic reactant, solvent and initiator can be brought
23 together in any suitable manner. The important factors are
24 intimate contact of the high molecular weight olefin and
25 acidic reactant in the presence of a free-radical producing
26 material.

27
28 Although the following description shows the use of poly-
29 isobutene (PIB), maleic anhydride (MA) and polyisobutenyl
30 succinic anhydride (PIBSA), it is intended to be merely
31 exemplary and the disclosure is intended to apply equally
32 well to other high molecular weight olefins, unsaturated
33 acidic reactants and the reaction products therefrom.
34 Moreover, the following exemplary polyPIBSA disclosure is

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01 intended to apply equally well to the copolymer reaction
02 product of any of the unsaturated acidic reactants and high
03 molecular weight olefins described herein.

04

05 The reaction can be run either batchwise or continuously.
06 The reaction temperature range is about 90°C to 210°C and
07 preferably about 130°C to 150°C. The reactor temperature
08 effects the molecular weight distribution, and this can
09 influence the ratio of maleic anhydride to polybutene that
10 is fed to the reactor. Theoretically the maleic anhydride
11 charge can range from 1 to 2 moles of maleic anhydride per
12 mole of methyl vinylidene isomer of PIB. Typically, the
13 free radical initiator is charged at 0.1 moles initiator per
14 1.0 moles maleic anhydride, although this can vary. The
15 reaction can be carried out at atmospheric pressure,
16 although at the higher temperature range it may be desirable
17 to pressurize the reactor slightly (i.e., 10 psig) to
18 suppress the loss of maleic anhydride to the vapor phase.
19 Neutral oil can be used to reduce the viscosity of the
20 mixture, but this can be deleterious to the reaction rate
21 and productivity of the reactor.

22

23 If the reaction is run batchwise, PIB and polyPIBSA from a
24 previous run are charged to the reactor. Thermal process
25 PIBSA or chlorination process PIBSA may also be used in lieu
26 of or in addition to polyPIBSA. The ratio of PIB to
27 polyPIBSA should be such as to assure complete solubility of
28 maleic anhydride in the mixture at reaction conditions. If
29 polyPIBSA is not added at a sufficient level so as to
30 maintain total maleic anhydride solubility, the rate of
31 reaction can be negatively affected, and the formation of
32 resin may be likely. To maximize reactor productivity, the
33 minimum amount of polyPIBSA that is necessary to maintain
34 total solubility of the maleic anhydride charge should be

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01 used. The reactor is stirred and heated to the desired
02 reaction temperature, and the maleic anhydride and free
03 radical initiator are added at the appropriate time/times
04 during this step. Reaction times will vary with temper-
05 ature, concentration of reactants, and types of free radical
06 initiators. Reactions performed at 140°C, for example, were
07 nearly complete according to ^{13}C NMR in roughly two hours.
08 When the reaction is complete, removal of any unreacted
09 maleic anhydride can be accomplished by increasing the
10 reactor temperature to 150°C to 250°C, preferably 180°C to
11 200°C, while applying sufficient vacuum. This procedure
12 also tends to decompose any remaining free radical initia-
13 tor. Another method for removal of unreacted maleic
14 anhydride is the addition of a solvent (e.g., hexane) which
15 solubilizes the polyPIBSA and precipitates the maleic
16 anhydride. The mixture then is filtered to remove the
17 maleic anhydride followed by stripping to remove the
18 solvent.

19

20 If the reaction is run continuously, a continuous stirred
21 tank reactor (CSTR) or series of such reactors can be used.
22 Reaction conditions should be selected to maintain the bulk
23 concentration of polyPIBSA at a sufficient level to maintain
24 maleic anhydride solubility in the reactor or series of
25 reactors. A continuous reactor is thought to be particu-
26 larly advantageous for reactions carried out at the lower
27 temperature range. As the temperature is reduced, the
28 maleic anhydride solubility in the polyPIBSA/polybutene
29 mixture decreases and this necessitates that the polyPIBSA
30 concentration be increased or the maleic anhydride concen-
31 tration be decreased so that total solubility of the maleic
32 anhydride is maintained. In a batch process an increase in
33 the initial charge of polyPIBSA can result in a decrease in
34 reactor productivity. Likewise, decreasing the maleic

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01 anhydride charge or extending the addition of maleic
02 anhydride over a time period can decrease reactor produc-
03 tivity. On the other hand, in a CSTR at steady state con-
04 ditions the polyPIBSA concentration in the bulk mixture is
05 not only constant, but it is essentially the same the
06 product exiting the reactor. Therefore, the polyPIBSA
07 concentration in a CSTR is at a maximum (equal to the
08 polyPIBSA product for a single stage CSTR) when compared to
09 a simple batch process where the all polybutene is charged
10 at the beginning of the reaction and the polyPIBSA concen-
11 tration is at a minimum.

12
13 For the continuous reactor, the temperature can range from
14 90°C to 210°C and preferably from 130°C to 150°C. PIB,
15 maleic anhydride, and free-radical initiator can be fed
16 continuously at appropriate rates so as to maintain a
17 certain level of conversion of the reactants to polyPIBSA.
18 It is envisioned that the product stream from the reactor
19 then is heated to a temperature in the range of 150°C to
20 250°C and preferably in the range from 180°C to 200°C to
21 strip off any unreacted maleic anhydride and to decompose
22 any remaining free-radical initiator. Vacuum can also be
23 sued to facilitate removal of the unreacted maleic
24 anhydride. It is envisioned that a wiped film evaporator or
25 similar types of equipment may be suitable for this type of
26 operation.

27
28 In one envisioned embodiment, the reaction product of an
29 unsaturated acidic reactant and a high molecular weight,
30 high vinylidene-containing olefin is further reacted
31 thermally. In this embodiment, any unreacted olefin,
32 generally the more hindered olefins, i.e., the non-vinyl-
33 idene, that do not react readily with the unsaturated acidic
34 reactant under free radical conditions are reacted with

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01 unsaturated acidic reactant under thermal conditions, i.e.,
02 at temperatures of about 180° to 280°C. These conditions
03 are similar to those used for preparing thermal PIBSA.
04

05 The reaction solvent, as noted above, must be one which
06 dissolves both the acidic reactant and the high molecular
07 weight olefin. It is necessary to dissolve the acidic
08 reactant and high molecular weight olefin so as to bring
09 them into intimate contact in the solution polymerization
10 reaction. It has been found that the solvent must also be
11 one in which the resultant copolymers are soluble.
12

13 It has been found that a small amount of haze or resin,
14 typically less than one gram per liter, is observed at the
15 end of reaction. Accordingly, the reaction mixture is
16 typically filtered hot to remove this haze or resin.
17

18 In general, after the reaction is deemed complete, for
19 example, by NMR analysis, the reaction mixture is heated to
20 decompose any residual initiator. For a di(t_i-butyl)
21 peroxide initiator, this temperature is typically about
22 160°C.
23

24 The isolated copolymer may then be reacted with a polyamine
25 to form a polymeric succinimide. The preparation and
26 characterization of such polysuccinimides and their treat-
27 ment with other agents to give other dispersant compositions
28 is described herein.
29

30 A(4) Preferred Copolymers

31

32 Preferred copolymers prepared by the present process include
33 those where an unsaturated acidic reactant, most preferably
34 maleic anhydride, is copolymerized with a "reactive"

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01 polyisobutene, in which at least about 50 percent or more of
02 the polyisobutene comprises the alkylvinylidene, more
03 preferably, the methylvinylidene, isomer, to give a
04 "polyPIBSA".

05

06 Preferred are polyPIBSAs wherein the polyisobutyl group has
07 an average molecular weight of about 500 to about 5000, more
08 preferably from about 950 to about 2500. Preferred are
09 polyPIBSAs having an average degree of polymerization of
10 about 1.1 to about 20, more preferably from about 1.5 to
11 about 10.

12

13

14

B. POLYSUCCINIMIDES

15 As noted above, polyamino polysuccinimides may be convenien-
16 tly prepared by reacting a copolymer made by the present
17 process with a polyamine. Polysuccinimides which may be
18 prepared include monopolysuccinimides (where a polyamine
19 component reacts with one succinic group), bis-polysuccini-
20 mides (where a polyamine component reacts with a succinic
21 group from each of two copolymer molecules), higher succi-
22 nimides (where a polyamine component reacts with a succinic
23 group from each of more than 2 copolymer molecules) or
24 mixtures thereof. The polysuccinimide(s) produced may
25 depend on the charge mole ratio of polyamine to succinic
26 groups in the copolymer molecule and the particular poly-
27 amine used. Using a charge mole ratio of polyamine to
28 succinic groups in copolymer of about 1.0, predominately
29 monopolysuccinimide is obtained. Charge mole ratios of
30 polyamine to succinic group in copolymer of about 1:2 may
31 produce predominately bis-polysuccinimide. Higher poly-
32 succinimides may be produced if there is branching in the
33 polyamine so that it may react with a succinic group from
34 each of greater than 2 copolymer molecules.

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01 The copolymers made by the present process, including
02 preferred copolymers such as polyPIBSA, may be post-treated
03 with a wide variety of other post-treating reagents. U.S.
04 Patent No. 4,234,435, the disclosure of which is incorpo-
05 rated herein by reference, discloses reacting succinic
06 acylating agents with a variety of reagents to give post-
07 treated carboxylic acid derivative compositions which are
08 useful in lubricating oil compositions.

09

10

C. LUBRICATING OIL COMPOSITIONS

11

12 The copolymers, polysuccinimides and modified polysuccini-
13 mides described herein are useful as detergent and disper-
14 sant additives when employed in lubricating oils. When
15 employed in this manner, these additives are usually present
16 in from 0.2 to 10 percent by weight to the total composition
17 and preferably at about 0.5 to 8 percent by weight and more
18 preferably at about 1 to about 6 percent by weight. The
19 lubricating oil used with these additive compositions may be
20 mineral oil or synthetic oils of lubricating viscosity and
21 preferably suitable for use in the crankcase of an internal
22 combustion engine. Crankcase lubricating oils ordinarily
23 have a viscosity of about 1300 CST 0°F to 22.7 CST at 210°F
24 (99°C). The lubricating oils may be derived from synthetic
25 or natural sources. Mineral oil for use as the base oil in
26 this invention includes paraffinic, naphthenic and other
27 oils that are ordinarily used in lubricating oil composi-
28 tions. Synthetic oils include both hydrocarbon synthetic
29 oils and synthetic esters. Useful synthetic hydrocarbon
30 oils include liquid polymers of alpha olefins having the
31 proper viscosity. Especially useful are the hydrogenated
32 liquid oligomers of C₆ to C₁₂ alpha olefins such as 1-decene
33 trimer. Likewise, alkyl benzenes of proper viscosity, such
34 as didodecyl benzene, can be used.

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01 Blends of hydrocarbon oils with synthetic oils are also
02 useful. For example, blends of 10 to 25 weight percent
03 hydrogenated 1-decene trimer with 75 to 90 weight percent
04 150 SUS (100°F) mineral oil gives an excellent lubricating
05 oil base.

06

07 Lubricating oil concentrates are also envisioned. These
08 concentrates usually include from about 90 to 10 weight
09 percent, preferably from about 90 to about 50 weight
10 percent, of an oil of lubricating viscosity and from about
11 10 to 90 weight percent, preferably from about 10 to about
12 50 weight percent, of an additive described herein. Typi-
13 cally, the concentrates contain sufficient diluent to make
14 them easy to handle during shipping and storage. Suitable
15 diluents for the concentrates include any inert diluent,
16 preferably an oil of lubricating viscosity, so that the
17 concentrate may be readily mixed with lubricating oils to
18 prepare lubricating oil compositions. Suitable lubricating
19 oils which can be used as diluents typically have viscosi-
20 ties in the range from about 35 to about 500 Saybolt
21 Universal Seconds (SUS) at 100°F (38°C), although an oil of
22 lubricating viscosity may be used.

23

24 Other additives which may be present in the formulation
25 include rust inhibitors, foam inhibitors, corrosion
26 inhibitors, metal deactivators, pour point depressants,
27 antioxidants, and a variety of other well-known additives.

28

29 It is also contemplated that the additives described herein
30 may be employed as dispersants and detergents in hydraulic
31 fluids, marine crankcase lubricants and the like. When so
32 employed, the additive is added at from about 0.1 to 10
33 percent by weight to the oil. Preferably, at from 0.5 to 8
34 weight percent.

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01 D. FUEL COMPOSITIONS

02

03 When used in fuels, the proper concentration of the additive
04 necessary in order to achieve the desired detergency is
05 dependent upon a variety of factors including the type of
06 fuel used, the presence of other detergents or dispersants
07 or other additives, etc. Generally, however, the range of
08 concentration of the additive in the base fuel is 10 to
09 10,000 weight parts per million, preferably from 30 to 5000
10 parts per million of the additive per part of base fuel. If
11 other detergents are present, a lesser amount of the addi-
12 tive may be used. The additives described herein may be
13 formulated as a fuel concentrate, using an inert stable
14 oleophilic organic solvent boiling in the range of about
15 150° to 400°F. Preferably, an aliphatic or an aromatic
16 hydrocarbon solvent is used, such as benzene, toluene, xylene
17 or higher-boiling aromatics or aromatic thinners. Aliphatic
18 alcohols of about 3 to 8 carbon atoms, such as isopropanol,
19 isobutylcarbinol, n-butanol and the like, in combination
20 with hydrocarbon solvents are also suitable for use with the
21 fuel additive. In the fuel concentrate, the amount of the
22 additive will be ordinarily at least 5 percent by weight and
23 generally not exceed 70 percent by weight, preferably from 5
24 to 50 and more preferably from 10 to 25 weight percent.

25

26 The following examples are offered to specifically illus-
27 trate this invention. These examples and illustrations are
28 not to be construed in any way limiting the scope of this
29 invention.

30

31

32

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01

EXAMPLES

02

03

Example 1 (Comparative)

04

Preparation of Polyisobutyl-24 PolyPIBSA

05

06 To a 12-liter, 3-neck flask equipped with an overhead
07 stirrer, thermometer, condenser, and heating mantle under
08 nitrogen atmosphere was added 5,000 grams (5.265 mole) of
09 polyisobutene of about 950 molecular weight having the trade
10 name ULTRAVIS-10 obtained from BP Chemicals wherein the
11 methylvinylidene isomer comprised about 70% of the total
12 composition, 1547.1 grams (15.79 mole) maleic anhydride, and
13 2,500 ml chloroform. The mixture was heated to reflux, and
14 to this was added 67.21 grams (0.41 mole) 22'-azobis
15 (2-methyl-propionitrile) ("AIBN"). The mixture was refluxed
16 for two hours at which time an additional 67.21 grams of
17 AIBN was added. This was followed by another two hours of
18 reflux and a third charge (66.58 grams) of AIBN. A total of
19 201 grams (1.2 mole) of AIBN was added. The reaction mix-
20 ture was refluxed a total of 20 hours, and then allowed to
21 cool. Two layers formed. The lower phase which contained
22 mostly chloroform and unreacted maleic anhydride was dis-
23 carded. The upper layer which contained mainly product and
24 unreacted polyisobutene was separated. Solvent and maleic
25 anhydride were removed in vacuo. A total of 4,360 grams of
26 product having a saponification number of 40.4 was
27 recovered.

28

29

Example 2 (Comparative)

30

Preparation of Polyisobutyl-24 PolyPIBSA

31

32 To a 1-liter 3-neck flask equipped with a thermometer, over-
33 head stirrer, nitrogen inlet and water condenser, was added
34 165.02 grams (0.174 mole) polyisobutylene (ULTRAVIS-10 from

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01 BP Chemicals) and 105 ml dichloroethane, then 16.4 grams
02 (0.167 mole) maleic anhydride were added. The resulting
03 mixture was heated to about 45°C, and 3.3 grams (0.017 mole)
04 tert-butylperbenzoate was added. The resulting mixture was
05 heated to reflux (83°C). The reaction mixture was heated
06 (with stirring) for a total of 30 hours. The reaction mix-
07 ture was allowed to cool. The solvent was removed in vacuo.
08 Unreacted maleic anhydride was removed by heating the resi-
09 due to 150°C at 0.1 mm Hg vacuum. A total of 176.0 grams
10 product was obtained, which had an average molecular weight
11 of about 5000. The conversion was about 60%. The
12 saponification number was 73.3.

13

14 Examples 3 to 15 and Examples 1C to 5C (Comparative)

15

16 Table I tabulates additional preparations following the
17 basic synthetic procedure outlined in Examples 1 and 2.
18 Table I lists the reactants, reaction temperature, time and
19 solvent, and free radical initiator used.

20

21 Example 12 was prepared using polyisobutene of about 1300
22 molecular weight having the trade name ULTRAVIS-30 obtained
23 from BP chemicals wherein the methylvinylidene isomer
24 comprised about 70% of the total composition.

25

26 Comparison Examples 1C to 5C were prepared using a polyiso-
27 butylene of about 950 molecular weight prepared with
28 AlCl_3 catalysis having the trade name Parapol 950 obtained
29 from Exxon Chemical.

30

31

32

33

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TABLE I

Product of Example No.	Polybutene (g)	Maleic Anhydride (g)	Solvent (ml)	Initiator* (g)	Temp °C	Time Hrs.
2	Ultravis-10 (165.09)	16.4	Dichloroethane (105)	TBPP (3.3)	83	30
3	Ultravis-10 (384.6)	119	Toluene (250)	AIBN (15.5)	110	6
4	Ultravis-10 (330)	32.3	Chlorobenzene (210)	DTBP (5.8)	138	30
5	Ultravis-10 (5000)	1547	Dichloroethane (2500)	AIBN (200)	83	13
6	Ultravis-10 (384.6)	119	Chloroform (250)	AIBN (15.5)	74	24
7	Ultravis-10 (384.6)	119	Methylene Chloride (250)	AIBN (15.5)	40	94
8	Ultravis-10 (330)	32.3	Toluene (210)	DTBP (5.8)	110	30
9	Ultravis-10 (330)	32.3	Xylene (210)	DTBP (5.8)	144	39
10	Ultravis-10 (330)	32.3	Xylene (210)	DTBP (5.8)	114	4
11	Ultravis-10 (330)	32.3	Toluene (210)	DTBP (5.8)	110	4
12	Ultravis-30 (217.1)	16.4	Dichloroethane (105)	TBPP (3.3)	83-184	26
13	Ultravis-10 (3350)	328.3	Chlorobenzene (1600)	DTBP (42.6)	138	28

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TABLE I (Cont'd)

Product of Example No.	Polybutene (g)	Maleic Anhydride (g)	Solvent (ml)	Initiator* (g)	Temp °C	Time Hrs.
14	Ultravis-10 (5000)	515.8	Chloroform (3000)	TBPB (102.8)	72	54
15	Ultravis-10 (10,000)	1031	Chloroform (6000)	TBPB (205.6)	72 then 140	48 2
1C	Parapol 950 (384.6)	119	Toluene (250)	AIBN (15.5)	110	6
2C	Parapol 950 (76.4)	23.8	Dichloroethane (50)	AIBN (2.33)	83	4
3C	Parapol 950 (330)	32.3	Toluene (210)	DTBP (5.8)	110	30
4C	Parapol 950 (330)	32.3	Xylene (210)	DTBP (5.8)	114	30
5C	Parapol 950 (330)	32.3	Chlorobenzene (210)	DTBP (5.8)	138	30

* AIBN = 2,2'-azobis (2-methyl-propionitrile); DTBP = ditertbutyl peroxide; TBPB = tertbutyl peroxybenzoate

** Molecular weight 1300

Example 16

A 500-ml, 3-necked flask was charged with 100g of a polyPIBSA/polybutene mixture (prepared according to the method of Example 5) which comprised about 38 weight percent polyPIBSA and about 62 weight percent (0.0653 mol) unreacted polyisobutene (of which about 68 weight percent (0.0444 mol) comprised the methylvinylidene isomer). The mixture was heated to 70°C. Then, 8g (0.0816 mol) maleic anhydride and 1.7g (0.0116 mol) di-tert-butyl peroxide were added to the

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01 mixture. The mixture was stirred and heated to 150°C for
02 5 hours. After allowing the mixture to cool, 150 ml hexane
03 was added to precipitate unreacted maleic anhydride which
04 was then removed by filtration. The hexane was removed by
05 stripping for 4 hours at 36 mm Hg (abs) at 90°C. The
06 filtered product had an unreacted maleic anhydride content
07 of 0.08 weight percent, as determined by gas chromatography.
08 The saponification number of the final product was deter-
09 mined to be 84 mg KOH/g sample. The amount of unreacted
10 polybutene was determined to be 28.2% by column
11 chromatography.

12

13

Example 17A

14

15 A 22-liter, 3-necked flask was charged with 3752g (3.95 mol)
16 of polyisobutene (BP Ultravis 10) and 2800g of a polyPIBSA/-
17 polyisobutene mixture (prepared according to Example 13)
18 which comprised about 57 weight percent polyPIBSA and about
19 43 weight percent (1.27 mol) unreacted polyisobutene. The
20 mixture was heated to 91°C; then 14g (0.143 mol) maleic
21 anhydride and 2.7g (0.0185 mol) di-tert-butyl peroxide
22 (DTBP) were added. A slight exotherm was noticed where the
23 temperature increased to 147°C. The mixture was stirred and
24 heated at 140°C for one hour. After standing at room tem-
25 perature overnight, the mixture was heated to 140°C and 378g
26 (3.86 mol) maleic anhydride and 56.7g (0.388 mol) of DTBP
27 were added. The mixture was stirred and heated at 140°C for
28 6.5 hours. The mixture was allowed to cool to ambient tem-
29 perature overnight. The mixture was heated to 80°C and
30 vacuum was applied at 28 inches Hg (vac); the temperature
31 was increased to 200°C. The mixture was stripped at 200°C
32 and 28 inches Hg (vac) for 2 hours to remove any unreacted
33 maleic anhydride. Analysis of the final product by proton
34 NMR showed that a significant amount of the polybutene

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01 methylvinylidene isomer had disappeared along with the
02 maleic anhydride.

03

04

Example 17B

05

06 A 22-liter, 3-necked flask was charged with 8040g (8.46 mol)
07 polyisobutene (BP Ultravis 10) and 6000g of a polyPIBSA/-
08 polybutene mixture prepared according to Example 17A. The
09 mixture was heated to 109°C, then 840g (8.57 mol) maleic
10 anhydride and 126g (0.863 mol) DTBP were added. The
11 resulting mixture was stirred and heated at 140°C for 5.25
12 hours. The mixture was cooled to ambient temperature. The
13 mixture was then heated to 128°C with stirring and an addi-
14 tional 153g (1.561 mol) maleic anhydride and 23g (0.158 mol)
15 DTBP were added. The mixture was stirred and heated at
16 140°C for 3.5 hours and then an additional 153g (1.561 mol)
17 maleic anhydride and 11.8g (0.0808 mol) DTBP were added.
18 The mixture was stirred and heated at 140°C for an addi-
19 tional 3.67 hours. The mixture was cooled to ambient
20 temperature. The mixture was then stirred and heated at
21 186°C for one hour while vacuum was applied to strip the
22 unreacted maleic anhydride from the product. The product
23 had a saponification number of 85.8 mg KOH/g. Inspection of
24 the proton NMR spectrum of the final product indicated that
25 the polybutene methyl vinylidene isomer was significantly
26 depleted and that the maleic anhydride was totally consumed.

27

28

Example 18

29

30

Preparation of PolyPIBSA TETA

31

Polysuccinimide with a Low Degree of Polymerization

32

33 To a 5-liter flask equipped with a heating mantle, overhead
34 stirrer and Dean Stark trap under nitrogen sweep, was added

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01 1000 g polyPIBSA prepared according to Example 17B
02 (saponification number 85.8, molecular weight about 2500)
03 and 999 g Chevron 100NR diluent oil. The mixture was heated
04 to 60°C; then 75.78 g triethylene tetraamine (TETA) was
05 added. The mixture was heated to 160°C and kept at tempera-
06 ture for 4 hours. A total of 7.0 ml water was recovered
07 from the Dean Stark trap. The reaction mixture was then
08 maintained at 160°C under vacuum for 2 hours. The reaction
09 mixture was allowed to cool. Obtained was 2018.2 g of
10 product having %N=1.35.

11

12

Example 19

13

14

Preparation of PolyPIBSA HPA

15

Polysuccinimide With a Low Degree of Polymerization

16

17 To a 5-liter flask equipped with a heating mantle, overhead
18 stirrer and Dean Stark trap (under nitrogen sweep) was added
19 1000 g polyPIBSA prepared according to Example 17B
20 (saponification number 85.8 molecular weight 2500) and 932
21 Chevron 100NR diluent oil. The mixture was heated to 60°C;
22 to this was added 142.45 g heavy polyamine ("HPA") No. X
23 obtained from Union Carbide Corporation. The mixture became
24 very thick. The reaction mixture was heated to 165°C and
25 maintained at that temperature for 4 hours; the mixture
26 became less viscous. Then the reaction mixture was heated
27 at 165°C under vacuum for 2 hours. The mixture was allowed
28 to cool. Obtained was the above-identified product having
29 %N=2.23.

30

31

Example 20 (Comparative)

32

33 An experiment was performed in a manner similar to
34 Examples 17A and 17B, but in the absence of any added

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01 oligomeric copolymer solvent. The resulting mixture, upon
02 heating, formed a significant amount of maleic anhydride
03 (MA) resin, as indicated by total disappearance of the MA
04 peak in the proton NMR, while still leaving a large amount
05 of methyl vinylidene protons. Moreover, MA resin formation
06 was evidenced by the product being stuck to the reactor
07 walls and the formation of tar.

08
09 Example 21

10 Proton NMR Analysis of Reaction
11 of Polyisobutene with MA
12

13 The reaction of PIB with MA can be monitored by proton NMR.
14 The MA peak in deuteriochloroform is located at 7.07 ppm and
15 the methyl vinylidene olefin hydrogens are at 4.61 and
16 4.87 ppm. Disappearance of these peaks, especially the PIB
17 vinylidene peaks, indicates copolymerization with the MA.
18 IR can also be used to confirm that copolymerization is
19 occurring. Generally, the reaction is run until the MA
20 olefin peak disappears and the methyl vinylidene peaks have
21 significantly decreased.

22
23 Example 22

24 Saponification Number of PIBSA and PolyPIBSA
25

26 Approximately one gram of sample is weighed and dissolved in
27 30 ml xylene in a 250-ml Erlenmeyer flask at room tempera-
28 ture. Unless otherwise noted, the polyPIBSA product samples
29 were filtered at about reaction temperature to remove any MA
30 hydrolysis product (i.e., fumaric acid) and any poly MA
31 resin.

32
33 Twenty-five ml of KOH/methanol is added to the xylene
34 solution. A reflux condenser is attached and the mixture is

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01 heated to reflux using a hotplate/stirrer and held at reflux
02 for 20 minutes. A ceramic spacer is placed beneath the
03 flask, and 30 ml of isopropyl alcohol is added through the
04 condenser. The sample is then cooled to about room temper-
05 ature and back titrated with 0.5 Normal HCl, using a Metrohm
06 670 auto titrator and a Dosimat 665 pump system.

07

08 Comparisons with blanks provide the saponification number
09 (SAP number), which is mg of KOH/gm of sample.

10

11

Examples 23-25

12

13 Examples 23-25 were carried out following the general
14 procedure of Examples 16, 17A and 17B. The results are
15 shown in Table II.

16

17 In Example 24, proton NMR showed a significant consumption
18 of polyisobutene methyl vinylidene isomer and maleic
19 anhydride. In Example 25, the maleic anhydride and free
20 radical initiator were added by slugs.

21

22

Example 26

23

24 A reaction mixture containing 350 grams of a 45 weight
25 percent polyPIBSA and 55 weight percent unreacted polyiso-
26 butene mixture having a SAP Number of 34 was combined with
27 150 grams BP ULTRAVIS 30, a high vinylidene polyisobutene
28 having an average molecular weight of about 1300 and 176
29 grams of a Chevron 100 neutral lubricating oil. The mixture
30 was heated to 50°C. Twenty-two (22) grams of maleic
31 anhydride and 5 grams of t-butylperoxy-2-ethyl hexanoate
32 (t-butyl peroctoate) were added. The reaction temperature
33 was raised to 90°C and held at this temperature for 4 hours.

34

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01 A product with a SAP Number of 26 was produced. Proton NMR
02 indicated a very slow reaction rate.

03

04

Example 27

05

06 A reaction mixture containing 500 grams of a 45 weight
07 percent polyPIBSA and 55 weight percent unreacted polyiso-
08 butene mixture having a SAP Number of 34 was combined with
09 214 grams BP ULTRAVIS 30, a high vinylidene polyisobutene
10 having an average molecular weight of about 1300. The
11 mixture was heated to 110°C and 31.4 grams of maleic
12 anhydride was added. Every 15 minutes starting from the MA
13 addition time, 6.53 grams of 100 neutral oil and 0.73 grams
14 of t-butylperoxy-2-ethyl hexanoate (t-butyl peroctoate) were
15 added. Additions were continued for the first 2 hours and
16 30 minutes. Thereafter the reaction was held at 110°C for
17 5.5 hours. This produced a product which had a SAP Number
18 of 31. Proton NMR showed a slow reaction rate.

19

20

Example 28

21

22 A reaction mixture containing 464 grams of a 45 weight
23 percent polyPIBSA and 55 weight percent unreacted polyiso-
24 butene mixture having a SAP Number of 34 was combined with
25 316 grams BP ULTRAVIS 30, a high vinylidene polyisobutene
26 having an average molecular weight of about 1300. The
27 mixture was heated to 120°C and 31.2 grams of maleic
28 anhydride and 5.85 grams of t-butylperoxy-2-ethyl hexanoate
29 (t-butyl peroctoate) were added. The reaction temperature
30 was raised to and held at 120°C for 6 hours. A product with
31 a SAP Number of 33 was produced.

32

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Example 29

01
02
03 A reaction mixture containing 259 grams of a 45 weight
04 percent polyPIBSA and 55 weight percent unreacted polyiso-
05 butene mixture having a SAP number of 34 was combined with
06 177 grams BP ULTRAVIS 30, a high vinylidene polyisobutene
07 having an average molecular weight of about 1300. The
08 mixture was heated to 130°C and 12.6 grams of maleic
09 anhydride and 3.32 grams of di-t-butylperoxide were added.
10 The reaction temperature was held at 130°C for 5 hours.
11 Then 5.1 grams of maleic anhydride and 0.7 grams of di-t-
12 butylperoxide were added. The temperature was raised to
13 140°C and then held these for 4.5 hours. The product had a
14 SAP Number of 41. Proton NMR showed a significant reduction
15 in polyisobutene methyl vinylidene isomer.

Example 30

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18
19 A reaction mixture containing 896 grams of polyPIBSA con-
20 taining some unreacted polybutene was combined with 1883
21 grams BP ULTRAVIS 30. The mixture was heated to 140°C and
22 142 grams of maleic anhydride and 21.2 grams of di-t-butyl-
23 peroxide were added. The reaction temperature was raised
24 and held at 140°C for 4 hours and then heated to 200°C for 2
25 hours. The product had a SAP Number of 49.

Example 31 (Comparative)

26
27
28
29 A reactor containing 721 grams BP ULTRAVIS 30 was heated to
30 140°C and 38.8 grams of maleic anhydride and 8.2 grams of
31 di-t-butylperoxide were added. This reaction was done in
32 the absence of added polyPIBSA solvent. The reaction tem-
33 perature was held at 140°C for 7 hours. An abundance of
34 tarry resin, believed to be derived from the maleic

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01 anhydride was evident. The mixture was filtered hot. The
02 product had a SAP number of 17 after the resin was filtered
03 out. The percent actives was 37%.

04

05

Example 32

06

07 This reaction shows that after the copolymer is formed,
08 unreacted PIB can be reacted with maleic anhydride to form
09 thermal PIBSA.

10

11 PolyPIBSA prepared in a manner similar to Example 17B having
12 a SAP Number of 86 was charged to a reactor and heated to
13 204°C. A molar equivalent of MA (43.3 g), relative to
14 unreacted non-vinylidene polybutene, of MA was added and the
15 mixture heated to 232°C and held at this temperature for
16 4 hours. The temperature was reduced to 210°C and the
17 pressure was reduced to 28 inches of mercury. The reduced
18 pressure and temperature was maintained for one hour. Then
19 the mixture was filtered. The product had a SAP Number
20 of 88. The results of Examples 26-32 are shown in Table II.

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TABLE II

Example	PIB MW	PIB Mole	MA Mole	Initiator Type	Init. Mole	PIB Grams	PolyPIBSA Grams	Wt PIB in Rr Mixture	Rx Temp °C	Rx Time Minutes	SAP Number	Wt Active
23	950	0.00	0.08	Di-t-Butyl Peroxide	0.12	0.0	100	0.0	150	300	90	71.8
24	950	3.95	4.00	Di-t-Butyl Peroxide	0.40	3752.0	2800.0	57.3	140	400	—	—
25	950	8.46	8.57	Di-t-Butyl Peroxide	0.86	8040.0	6000.0	53.5	140	620	76	77.2
26 ^a	1300	0.12	0.23	t-Butyl Peroctoate	0.02	150.0	350.0	22.2	90	240	26	—
27 ^b	1300	0.17	0.32	t-Butyl Peroctoate	0.03	214.5	500.0	27.5	110	330	31	—
28	1300	0.24	0.32	Di-t-Butyl Peroxide	0.04	315.8	463.8	40.5	120	240	33	—
29	1300	0.14	0.13	Di-t-Butyl Peroxide	0.03	176.9	259.0	40.6	130	450	41	—
30	1300	1.45	1.45	Di-t-Butyl Peroxide	0.15	1883.0	896.0	70.3	140	240	49	60.4
31	1300	0.55	0.40	Di-t-Butyl Peroxide	0.06	721.0	0.0	100.0	140	420	17	32.6
32	950	0.00	0.44	— None —	0.00	0.0	700.0	0.0	232	240	88	70.0

20 ^a The reaction mixture contained 176 grams of neutral lubricating oil (26 wt.% in reaction mixture).

21 ^b The reaction mixture contained 65.25 grams of neutral lubricating oil (8.4 wt.% in reaction mixture).

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01 WHAT IS CLAIMED IS:

02

03 1. A process for preparing an oligomeric copolymer of an
04 unsaturated acidic reactant and a high molecular weight
05 olefin having a sufficient number of carbon atoms such
06 that the resulting copolymer is soluble in lubricating
07 oil and wherein at least 20 weight percent of the total
08 olefin comprises an alkylvinylidene isomer, which
09 process comprises reacting the high molecular weight
10 olefin with the unsaturated acidic reactant in the
11 presence of a solvent which comprises the reaction
12 product of an unsaturated acidic reactant and a high
13 molecular weight olefin.

14

15 2. The process according to Claim 1, wherein the
16 unsaturated acidic reactant employed to produce either
17 the copolymer product or the solvent is of the formula:

18

19

20



21

22 wherein X and X' are each independently selected from
23 the group consisting of -OH, -Cl, -O-lower alkyl of 1
24 to 6 carbon atoms and when taken together, X and X'
25 are -O-.

26

27 3. The process according to Claim 1, wherein at least 50
28 percent of the total olefin employed to produce the
29 copolymer product comprises an alkylvinylidene isomer.

30

31 4. The process according to Claim 1, wherein the high
32 molecular weight olefin employed to produce either the
33 copolymer product or the solvent has an average
34 molecular weight of about 500 to about 5000.

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- 01 5. The process according to Claim 1, wherein the high
02 molecular weight olefin employed to produce either the
03 copolymer product or the solvent is polyisobutene.
04
- 05 6. The process according to Claim 1, wherein the
06 oligomeric copolymer produced has an average degree of
07 polymerization of about 1.5 to about 10.
08
- 09 7. The process according to Claim 1, wherein the acidic
10 reactant employed to produce the copolymer product is
11 maleic anhydride and the alkylvinylidene isomer
12 employed to produce the copolymer product is
13 methylvinylidene.
14
- 15 8. The process according to Claim 1, wherein the solvent
16 comprises the reaction product of maleic anhydride and
17 polyisobutene.
18
- 19 9. The process according to Claim 8, wherein the solvent
20 comprises thermal PIBSA or chlorination process PIBSA.
21
- 22 10. The process according to Claim 1, wherein the solvent
23 comprises the oligomeric copolymer product of said
24 process.
25
- 26 11. The process according to Claim 10, wherein the solvent
27 comprises polyPIBSA.
28
- 29 12. The process according to Claim 1, wherein the solvent
30 comprises either (a) an oligomeric copolymer of an
31 unsaturated acidic reactant and a high molecular weight
32 olefin, or (b) a monomeric adduct of an unsaturated
33 acidic reactant and a high molecular weight olefin in
34

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01 at least a one to one mole ratio of acidic reactant to
02 olefin; or a mixture thereof.
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INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US89/04282**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. C1⁴ C07C 55/00, 69/34; C07D 307/34; C10M 129/93

U.S. CL 562/590, 596; 560/190, 204; 549/233, 252; 252/56D

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System

Classification Symbols

U.S.

**562/590, 596; 560/190, 204; 549/233, 252
252/56D**

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
$\frac{X}{Y}$	US, A, 4,548,725 (BRIDGER) 22 October 1985 See entire document	<u>1-12</u> 1-12
$\frac{X}{Y}$	US, A 4,526,950 (GRAVA) 02 July 1985 See entire document	<u>1-12</u> 1-12
$\frac{X}{Y}$	US, A, 3,677,725 (ANDRESS, JR.) 18 July 1972 See entire document	<u>1-12</u> 1-12
$\frac{X}{Y}$	JP, A, 63-270671 (MITSUBISHI) 12 November 1988 See entire document	<u>1-12</u> 1-12
A	US, A, 4,359,325 (DAWANS ET AL) 16 November 1982 See entire document	1-12
A	US, A, 4,055,581 (HOPKINS ET AL) 25 October 1977 See entire document	1-12

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

Date of Mailing of this International Search Report

12 December 1989

09 FEB 1990

International Searching Authority

Signature of Authorized Officer

ISA/US

Brian McAvoy
Brian McAvoy

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